III.A.29 Thermochemically Stable Sealing Materials for Solid Oxide Fuel Cells

Objectives

- Develop 'invert' glasses with requisite properties and chemical stability for hermetic seals for solid oxide fuel cells (SOFCs).
- Develop processing techniques to fabricate hermetic seals for SOFC components.
- Demonstrate hermeticity and materials compatibility for seals under SOFC operational conditions.

Accomplishments

- Developed alkaline earth/zinc silicate glasses that form glass-ceramics with requisite thermal properties, including sealing temperatures at or below 900ºC and coefficients of thermal expansion (CTE) in the range of 10-12x10^{-6}/ºC.
- Demonstrated stability of promising sealing materials under SOFC operational conditions; e.g., stable CTE and low material volatility at temperatures up to 800ºC, for up to 100 days, in air and in wet forming gas.
- Produced hermetic seals between interconnect alloys and SOFC components, including Y-stabilized zirconia (YSZ) electrolytes and Ni-YSZ anodes, that pass He-leak tests after at least ten thermal cycles between 800ºC and room temperature.

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Introduction

Solid oxide fuel cells (SOFCs) are multi-layered structures formed primarily from high-purity metal oxide components, including an ionic conducting electrolyte, which generate electricity from the electrochemical oxidation of a fuel source. Within the SOFC stack, an effective seal must have a thermal expansion match to the fuel cell components, must be electrically insulating and must be thermochemically stable under the operational conditions of the stack. The seal should exhibit no deleterious interfacial reactions with other cell components, should be stable under both the high temperature oxidizing and reducing operational conditions, should be created at a low enough temperature to avoid damaging other cell components (under 900ºC for some materials), and should not migrate or flow from the designated sealing region during sealing or cell operation. In addition, the sealing system should be able to withstand thermal cycling between the operational temperature and room temperature. That is, thermal stresses that develop because of mismatches in the thermal contraction characteristics of the different SOFC materials must either be reduced to well below the failure strengths of the materials or must be relieved in some fashion. Finally, the sealing material should not adversely react with other SOFC components, to avoid producing deleterious interfacial reaction products or to volatilize and contaminate components elsewhere in the cell.

There have been many attempts to develop seals for planar SOFCs using a wide variety of glass and glass-ceramic compositions; see the review by Fergus [1] for many compositional examples. Most materials have drawbacks, including thermal expansion mismatches, excessive sealing temperatures, and long-term interfacial reactivity with other fuel cell materials. Thus, the seal has become a critical need for meeting the long-term operational milestones of the DOE fuel cell programs. The materials developed in the present project have unusual structural characteristics that contribute to a desirable set of thermal and chemical properties required for SOFC seals.

Approach

The glasses developed at the University of Missouri-Rolla (UMR) have relatively low silica contents (<45 mole%) and so possess molecular-level structures that are much less connected than conventional silicate glasses. These depolymerized structures contribute to desirably low viscosities at the sealing temperatures (900ºC), and lead to the formation of crystalline phases that possess relatively high CTEs and good thermal stabilities when the seals are crystallized to form glass-ceramics. The glass compositions are designed to avoid the formation of deleterious interfacial reaction products, like the Ba-chromates that form when BaO-containing glasses are sealed to ferritic interconnect alloys [2].

Results

Over fifty glass compositions have been prepared and evaluated. Many of the compositions have the requisite thermal properties required for SOFC seals (e.g., CTE match to SOFC components and sealing temperatures at or below 900ºC) and have been included in long-term materials stability experiments. The properties of two representative compositions are summarized in Table 1. Glass 27 has a CTE match to YSZ and glass 50 has a CTE that is intermediate to Cr-containing ferritic steel interconnect alloys and YSZ. Both glasses can be sealed and crystallized at or below 900ºC.

Of particular concern for SOFC seals is the long term stability of the properties of the sealing glasses. Figure 1 shows that the average CTE (over the temperature range from room temperature to 600ºC) of glass 27 and of glass 50 does not change with time at 800ºC for up to several months. X-ray diffraction studies (not shown) of the materials reveal that the dominant crystalline phases present in these glass-ceramics (Table 1) do not change with time at temperature. This phase stability is necessary if these glasses are to fulfill the fuel cell program requirements for functional SOFC lifetimes in excess of 10,000 hours at operational temperatures (700-800ºC).

Seals between YSZ and ferritic interconnect alloys have been prepared with the glasses developed in this project. Sealing materials include tapes and pastes prepared using materials and techniques based on commercial processes. Figure 2 shows a scanning electron micrograph of the interface between a glass 27 tape and a Cr-ferritic steel substrate after the seal was held at 750ºC for 100 hours. The crystalline microstructure of the glass-ceramic is evident in the micrograph, and there are no obvious heterogeneities at the glass/metal interface that indicate deleterious interfacial reactions. Ron Loehman (Sandia National Labs, Albuquerque, NM) has performed detailed analytical electron microscopic studies of interfaces between glass 27 and different SOFC component materials, including YSZ electrolytes, Ni-YSZ anodes, and several different Cr-containing ferritic interconnect alloys, and reports good wetting and good chemical compatibility of the glass with these different materials. For example, little Ni or Cr diffuses from the anode or the interconnect alloy, respectively, into the sealing glass after several days at elevated temperatures.

A series of simple seals have been fabricated and their hermeticity has been tested at room temperature using helium gas (2 psig). Figure 3 shows a photograph of one of these samples; this sample is about 25 mm

TABLE 1. Characteristics of UMR Sealing Glass-Ceramics

	Major crystalline phases	Sealing conditions	CTE after sealing
Glass 27	$CaSrAl_2SiO_7$, $Ca_2ZnSi_2O_7$	850ºC/2 hours	10.0×10^{-6}/ºC
Glass 50	$Sr_2Al_2SiO_7$, $CaSrSiO_4$	900ºC/5 min, then 800°C/2 hrs	11.5×10^{-6}/ºC

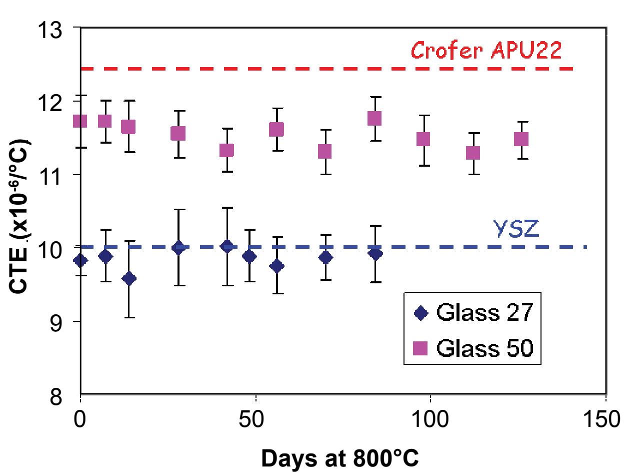

FIGURE 1. CTE for UMR Sealing Glass-Ceramics as a Function of Time in Air at 800ºC

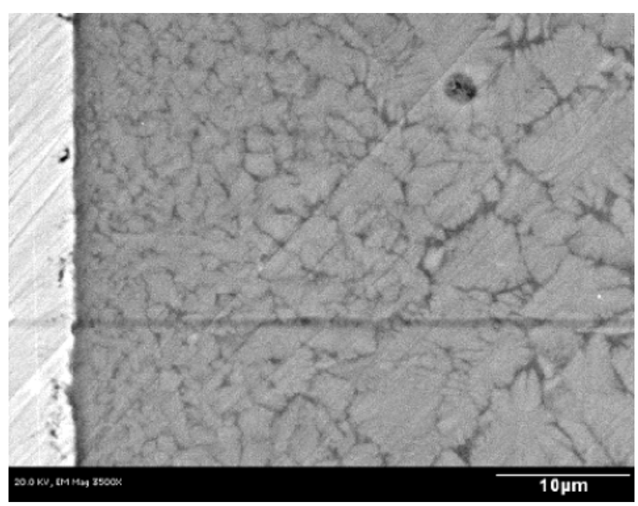

FIGURE 2. Scanning Electron Micrograph of the Interface of a Glass 27 (right)/Crofer APU 22 Seal after 100 Hours at 750ºC

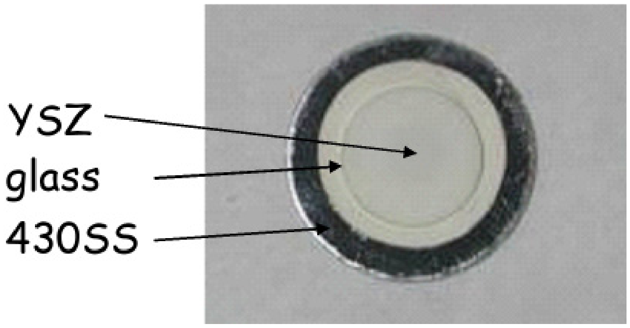

FIGURE 3. Optical Image of a Seal Couple Used for Helium Hermeticity Tests

in diameter. The seals were fabricated using glass tapes (PVB binder, 10 µm glass particles) fired in air to 850-900°C, between 430SS as the interconnect material and either YSZ (electrolyte) or Ni-YSZ (anode) substrates. These test samples were heated to 800°C, at 2°C/minute, in different atmospheres, held for 24 hours, then cooled to room temperature (-2°C/minute) where they were tested for hermeticity using helium gas at 2 psig. Samples that did not leak (hold 2 psig for four hours) were reheated for another 800°C/24 hour heat treatment, and cycled back to room temperature for another hermeticity test. Table 2 summarizes the results of some of these tests. Glasses fabricated both by UMR and by a commercial vendor have been evaluated.

TABLE 2. Summary of thermal cycling/hermeticity tests on sealed components. All tests were done using helium at room temperature, following the thermal treatment indicated.

Sealing materials	Test conditions	Number of cycles	Notes
430SS/glass 50/YSZ	800°C, 24 hours, wet forming gas	10	Still on test; glass prepared at UMR
430SS/glass 50/Ni-YSZ	800°C, 24 hours, wet forming gas	4	Still on test; glass prepared at UMR
430SS/glass 50/Ni-YSZ	800°C, 24 hours, air	10	Still on test; glass prepared at UMR
430SS/glass 50/YSZ	800°C, 24 hours, air	9	Failed after ninth cycle; glass prepared by commercial vendor
430SS/glass 50/Ni-YSZ	800°C, 24 hours, wet forming gas	4	Failed after fourth cycle; glass prepared by commercial vendor

Quantitative studies of SOFC glass crystallization behavior have been performed using differential thermal analysis (DTA) techniques developed at UMR [3]. By considering changes in the areas of crystallization exothermic peaks from DTA analyses of glass samples following isothermal heat treatments, the fraction of

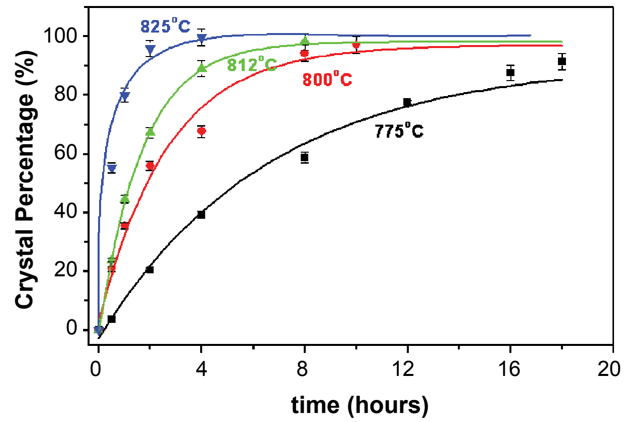

FIGURE 4. Crystallization Kinetics Curves for Glass 27 Obtained by Isothermal DTA Analyses

glass crystallized can be determined. An example of these analyses is shown in Figure 4 for glass 27 particles about 100 µm in diameter. These experiments have provided useful processing related information used to optimize sealing times and temperatures. In addition, these experiments have shown the effects of glass particle size on crystallization kinetics, and have shown how the addition of a second phase, intended to modify CTE, also affects crystallization kinetics.

Conclusions and Future Directions

- Promising 'invert' sealing glass compositions have been developed and evaluated.
- Hermetic seals have been fabricated and tested at room temperature after thermal treatments at operational temperatures.
- Glass crystallization kinetics have been evaluated using new DTA techniques.
- 'Invert' glass compositions for commercial suppliers and commercial processing techniques will be optimized.
- Viscosity and creep properties of sealing glasses will be characterized.
- We will complete characterization of long-term, high temperature interfacial reactions between glasses and SOFC components.
- We will produce and characterize 'at temperature' hermetic seals between SOFC component materials using new 'invert' glasses.

Special Recognitions & Awards/Patents Issued

1. R.K. Brow, S. T. Reis, G. M. Benson, "Glass and glass-ceramics for solid oxide fuel cell hermetic seals," US Patent Application, UM Disclosure No. 04UMR023 entitled "Glass and Glass-Ceramic Sealant Compositions," filed January 2005.

FY 2006 Publications/Presentations

1. S.T. Reis, R.K. Brow, "Designing Sealing Glasses for Solid Oxide Fuel Cells," Journal of Materials Engineering and Performance, 15[4], XXX-XXX, (2006)- (Proceedings of the ASM Materials Solution Conference, Fuel Cells: Materials, Processing and Manufacturing Technologies, Columbus, OH Oct. 18-20, 2004).

2. T. Zhang*, S. T. Reis, R. K. Brow, and C.S. Ray, "Crystallization Studies of SOFC Sealing Glasses," 3rd International Symposium on Solid Oxide Fuel Cell: Materials and Technology, 30th International Conference & Exposition on Advanced Ceramics & Composites, Cocoa Beach, FL, Jan. 22-27, 2006.

3. S.T. Reis, R.K. Brow, and T. Zhang, "Glass-Ceramic Seals for Solid Oxide Fuel Cells: Thermo-Phase Stability," 3rd International Symposium on Solid Oxide Fuel Cell: Materials and Technology, 30th International Conference & Exposition on Advanced Ceramics & Composites, Cocoa Beach, FL, Jan. 22-27, 2006.

4. S.T. Reis, R.K. Brow. P. Jasinski, and T. Zhang, "Properties of Glass-Ceramic Seals for Solid Oxide Fuel Cells," proceedings of the 3rd International Symposium on Solid Oxide Fuel Cells, 30th International Conference & Exposition on Advanced Ceramics & Composites, Cocoa Beach, FL, Jan. 22-27, 2006.; accepted for publication by the American Ceramic Society, 3/14/06.

5. T. Zhang, C.S. Ray, S.T.Reis, and R.K. Brow, "Isothermal Crystallization of Solid Oxide Fuel Cell Sealing glass by Differential Thermal Analysis," J. Amer. Ceram. Soc. (in preparation).

References

1. J.W. Fergus, *J. Power Sources*, 147 46-57 (2005).

2. C. S. Ray, T. Zhang, S. T. Reis and R. K. Brow, "Determining Kinetic Parameters for Isothermal Crystallization of Glasses," *Nucleation and Crystal Growth in Glasses and Liquids*, (submitted).

3. Z. Yang , J. W. Stevenson, and K. D. Meinhardt, *Solid State Ionics*, 160 213-222, (2003).